

# Possible Phosphorus-Bromine Synergy in Polyester-Cotton Fabrics Treated with Tetrabromobisphenol-A and Diammonium Phosphate

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**ABSTRACT:** Polyester/cotton fabrics were treated with tetrabromobisphenol-A (TBBA)/epichlorohydrin (EPI) aqueous solution, followed by being treated with diammonium phosphate (DAP)/urea solution. The optimum mole ratio of EPI to TBBA was determined. The synergism of TBBA and DAP was found to operate on the treated fabrics. The maximal synergism was obtained when the bath concentration of TBBA was equal to that of DAP. The mechanism of flame-retardancy was analyzed by thermogravimetry and residue number. The flame-retardancy of the polyester/cotton fabrics treated with TBBA/DAP was found operative mainly in the condensed-phase mechanism. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 172–177, 2002; DOI 10.1002/app.10292

**Keywords:** flame retardance; synergism; thermogravimetry; mechanism of flame retardance

## INTRODUCTION

Cotton is pyrolyzed to volatiles and carbonaceous char at a lower temperature than polyester. However, polyester melts and drips at temperatures above its melting point of 260°C, and hence, shows self-extinguishing properties. In the case of polyester/cotton-blended fabrics, the molten polymer cannot drip or flow away from the flame sources. It remains dispersed between the charred cotton that brings about the scaffolding effect.<sup>1</sup> Therefore, the flame-retardancy of polyester/cotton-blended fabrics is worse than cotton or polyester alone.<sup>2</sup> A flame-retardant finish of polyester/cotton-blended fabrics can be carried out by treating it with phosphorous compound alone or phosphorous compound plus bromine compound.

Durability of finish on treated fabrics is also very important in flame-retardant finishing of polyester/cotton-blended fabrics. In this study, the fabrics were treated with DAP and TBBA in a two-bath process, and flame-retardancy versus treatment condition or add-on of flame-retardant was investigated. The optimum mole ratio of EPI to TBBA was examined. Furthermore, the synergism of TBBA and DAP and the optimum ratio of two chemicals for the maximal synergistic effect were investigated. Finally, the flame-retardancy versus concentration of the flame retardant was analyzed.

## EXPERIMENTAL

### Fabrics

Polyester 50%/cotton 50% blended twill fabrics, the yarn count of which was Ne 16 in both warp and weft, were used. The fabric count was 104

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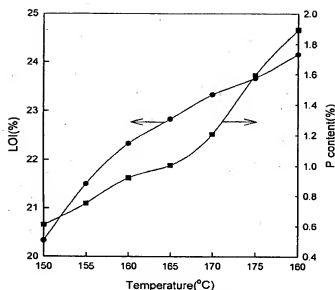


Figure 1 Phosphorus content and limiting oxygen index as a function of curing temperature for 3 min in DAP-treated fabrics. (DAP concentration: 25%; wet pickup: 65%).

ends/in. and 62 picks/in. Its weight was 251g/m<sup>2</sup>. Fabrics were obtained as dyed from a mill.

### Chemicals

Tetrabromobisphenol-A (TBBA; Great Lakes Co.) and diammonium phosphate (DAP; reagent grade) were used as flame retardants. Epichlorohydrin (EPI), methyl alcohol, urea, sodium hydroxide, and hydrogen peroxide were analytical grade. Sodium carbonate, Invadine LU (penetrating agent for TBBA), and Primazol NF (penetrating agent for DAP) were commercial grade.

### Treatment of Fabrics

To determine the optimum mole ratio of EPI to TBBA, the padding solution was prepared as follows: TBBA was dissolved in NaOH solution to be 15%, and EPI was dissolved in methyl alcohol. The two solutions were mixed so that the mole ratios of EPI to TBBA were 0.5, 1.0, 1.25, and 1.5. Invadine LU (0.2%, owf) was added to the mixed solution. The fabrics were padded by 2 dip-2 nip method with wet pickup of 65%, batched in the polyethylene bag for 48 h, and then dried at 85°C for 3 min. Treated fabrics were immersed in 1.5 g/L sodium carbonate solution of liquor ratio 40 : 1 at 70°C for 10 min and then washed thoroughly with cold water. The padding solutions of DAP/urea were prepared as follows: the mole ratio of

urea to DAP<sup>3</sup> was 1.0, and aqueous padding solutions with various concentrations of DAP ranging from 5 to 30% plus 0.2% (owf) Primazol NF were prepared. The fabrics were padded by 2 dip-2 nip method with wet pickup of 65%, dried at 85°C for 3 min, and cured at 160°C for 3 min. Treated fabrics were washed in 40°C water for 3 min and then rinsed thoroughly in cold water.

### Test and Analysis

#### Analysis of Elements

The Schöniger flask method<sup>4</sup> for bromine and phosphomolybdate method<sup>5</sup> for phosphorus were used, respectively.

#### Limiting Oxygen Index (LOI)

ASTM D 2863 (Tester: Suga Co., Japan) standard was used to measure the LOI<sup>6-8</sup>.

#### Thermogravimetric Analysis

A thermogravimetric analyzer (Model SSC-5200, Seiko Co., Japan) was used<sup>9</sup>. N<sub>2</sub> gas flow rate measured 100 ml/min and the temperature rise measured 10°C/min.

#### Residue Number<sup>10,11</sup>

$$Nr = \frac{R_f F}{R_u}$$

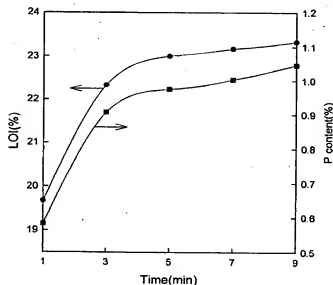


Figure 2 Phosphorus content and limiting oxygen index as a function of curing time at 160°C in DAP-treated fabrics. (DAP concentration: 25%; wet pickup: 65%).

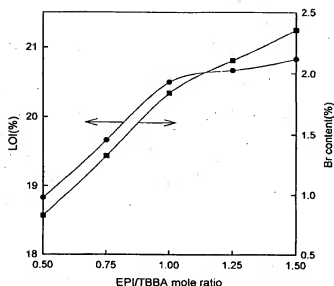


Figure 3 Bromine content and limiting oxygen index as a function of EPE/TBBA mole ratio in TBBA/EPI-treated fabrics. (TBBA concentration: 15%; wet pickup: 65%; batching time: 48 h).

where  $R_f$  is the wt % of residual char in the fabrics treated with flame-retardant;  $F$  is the weight fraction of fiber in the fabrics treated with flame-retardant; and  $R_u$  is the wt % of residual char in untreated fabrics.

#### Tensile Strength

ASTM D 1682-64 (1-in. raveled strip) was used to measure the tensile strength.

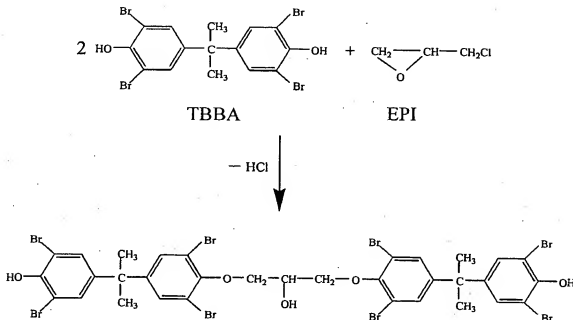
## RESULTS AND DISCUSSION

### Curing Temperature and Time for DAP Treatment

Figure 1 shows the phosphorus content and LOI as a function of curing temperatures ranging from 150 to 180°C for 3 min. The phosphorus content on treated fabrics increases as curing temperature increases. The LOI also increases almost linearly as curing temperature increases. The shade of treated fabrics shows yellowing above 160°C. The phosphorus content and the LOI of treated fabrics increase as curing time increases, as shown in Figure 2. However, not only their increment becomes small, but also the shade of treated fabrics shows yellowing above 3 min. From the results mentioned above, the curing condition hereafter was set to 160°C, 3 min.

### Optimum Mole Ratio of EPI to TBBA

The bromine content and LOI of treated fabrics increase as the mole ratio of EPI to TBBA increases, as shown in Figure 3. This indicates that the add-on of TBBA on treated fabrics increases as the amount of EPI increases. However, when the mole ratio of EPI to TBBA exceeds 1.0, the increment of LOI becomes small and treated fabrics stiffened. Hence, the optimum mole ratio of EPI to TBBA is considered 1.0. It is considered that TBBA reacts with EPI to form insoluble compounds on the fabrics, as shown in Scheme 1.



Scheme 1 Hypothetical structure of TBBA-EPI.

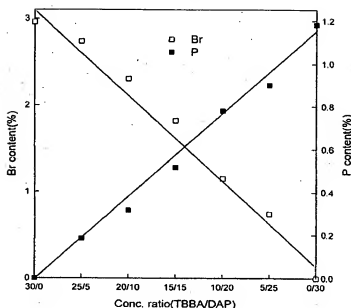


Figure 4 Bromine and phosphorus contents as a function of TBBA/DAP concentration ratio in treated fabrics. (Total concentration of TBBA and DAP: 30%; wet pickup: 65%).

#### TBBA-DAP Synergism

Figure 4 shows the bromine or phosphorus content on treated fabrics versus concentration ratio of TBBA/DAP when total concentration of TBBA and DAP in the padding solution is 30%. The bromine or phosphorus content on treated fabrics increases linearly as the concentration of TBBA or DAP in the padding solution increases. In Figure 5, the solid curve shows the LOI as a function of the concentration of TBBA/DAP, as mentioned in Figure 4. The broken line indicates the predicted LOI values. We see that the LOI is greater than that predicted on the basis of additivity of the individual flame-retardant component. In other words, it is evident that there exists TBBA-DAP synergism in flame-retardancy.<sup>12</sup> The weight ratio TBBA : DAP of 1 : 1 is found to yield the maximum synergistic effect.

#### LOI and Strength Retention of Treated Fabrics

When the fabrics are treated with the padding solutions containing TBBA/DAP, the percentage of which is 10/10, 15/15, 20/20, 25/25, and 30/30, their LOI value and tensile strength retention are 23.0, 24.8, 26.2, 27.7, 28.3, and 81, 80, 75, 77, and 74%, respectively. The tensile strength and LOI of untreated fabrics are 79.8 and 18.5 kg, respectively.

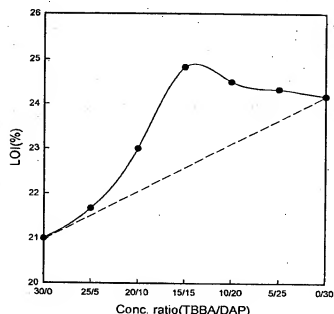


Figure 5 Limiting oxygen index as a function of TBBA/DAP concentration ratio in treated fabrics. (Total concentration of TBBA and DAP: 30%; wet pickup: 65%).

#### Analysis of Mechanism of Flame Retardancy

##### Thermogravimetric Analysis

Figure 6 shows that cotton fibers begin to be pyrolyzed at much lower temperature than polyester fibers. The temperature where the rate of pyrolysis reaches maximum is very different between two fibers. Furthermore, the residual char after pyrolysis is larger in polyester fiber than in cotton fibers. The curve (Experimental) indicates thermogravimetric curve of the sample consisting of 50% polyester and 50% cotton, whereas the

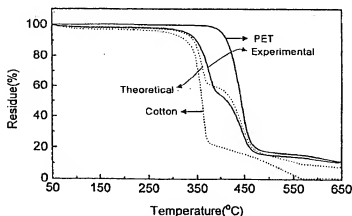


Figure 6 Comparison of thermogravimetric analysis curves for polyester 50%/cotton 50% blended fabrics with theoretical analysis curve.

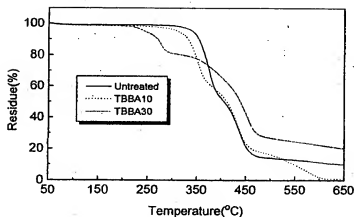


Figure 7 Thermogravimetric analysis curves for TBBA-treated fabrics.

curve (Theoretical) is the one from combining two curves of PET and cotton in the ratio of 50 : 50%. Two curves show some differences both in the range where the rate of pyrolysis is maximal and in the amount of residual char. This means there exists a certain interaction between two fibers when those are pyrolyzed together. Figures 7 and 8 show thermogravimetric curves of fabrics untreated or treated with TBBA or DAP, respectively. Pyrolysis of the fabrics treated with TBBA or DAP occurs earlier than that of untreated fabrics. Above a certain temperature, the rate of pyrolysis of treated fabrics becomes slower than that of untreated fabrics. The amount of residual char versus the add-on of TBBA does not show any tendency. This means that the gas-phase mechanism is mainly operative in the polyester/cotton fabrics treated with TBBA. However, the amount of residual char increases as the add-on of DAP increases. Therefore, the condensed-phase

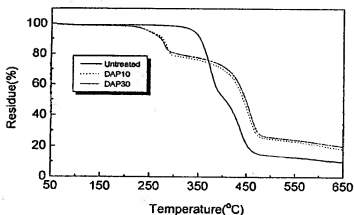


Figure 8 Thermogravimetric analysis curves for DAP-treated fabrics.

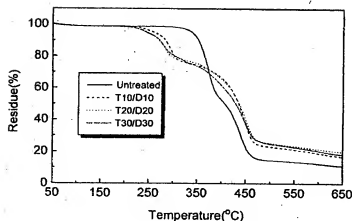


Figure 9 Thermogravimetric analysis curves for TBBA-DAP-treated fabrics.

mechanism is found operative in the polyester/cotton fabrics treated with DAP.<sup>12</sup> As shown in Figure 9, the condensed-phase mechanism mainly operates in the fabrics treated with TBBA/DAP combination, considering the residual char.

#### Residue Number

Pensa and Sello<sup>11</sup> suggested the concept of residue number to clarify the mechanism of flame-retardancy. In the condensed-phase mechanism, both the LOI and the residue number (Nr) increase as the add-on of the flame retardant on treated fabrics, whereas in the gas-phase mechanism, the LOI increases, but residue number does not increase. The fact that the condensed-phase mechanism mainly operates in the fabrics treated with TBBA/DAP combination is reconfirmed from the data in Table I, because both the LOI and the Nr of the fabrics treated with TBBA/DAP combination increase as the add-on of them increases.

#### CONCLUSION

Various processing conditions were investigated when polyester 50%/cotton 50% fabrics were pad-

Table I Residue Number and LOI of TBBA-DAP-Treated Fabrics

Sample	$R_f$ (%)	F	Nr	LOI
TBBA 10/DAP 10	16.74	0.87	1.76	23.0
TBBA 20/DAP 20	19.75	0.74	2.45	26.2
TBBA 30/DAP 30	17.98	0.61	2.70	28.3

Weight % of residual char in untreated fabrics ( $R_u$ ) = 10.91.

ded with TBBA/EPI aqueous solutions, batched, dried, and then treated with DAP/urea aqueous solutions by pad-dry-cure process to give a durable flame-retardancy. The optimum mole ratio of EPI to TBBA is found to be 1 : 1 in a viewpoint of bromine content, LOI value, and handle of treated fabrics. The optimum curing condition for treating DAP/urea is 160°C, 3 min, considering phosphorus content, LOI value, and shade of treated fabrics. The synergistic effect of TBBA and DAP is maximal when the concentrations of each component in each padding solution are equal to each other. The gas-phase mechanism is operative in the polyester/cotton fabrics with TBBA alone, whereas the condensed mechanism is operative when treated with DAP alone. However, the condensed-phase mechanism mainly operates when they are treated with TBBA/DAP combination.

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## LESSON 17 SPECIAL FINISHES

of the ignition source." The material that is flame resistant may be a polymer, fiber, or fabric.

2. Use of the terms *flame retardant* and *self-extinguishing* is discouraged (ASTM 1998, 23, 40). *Flame-retardant treated and flame-retarded treatment* are, however, acceptable terms and *flame retardant* is used in other countries. ASTM does not approve the use of the term *self-extinguishing* to describe a textile product because it is meaningful only when applied to specific circumstances.
3. A *thermally stable* material (fiber or polymer) is one that has a high decomposition temperature and is thus inherently flame resistant because of chemical structure (rather than through the presence of added flame-retardant treatments) (Clark and Tesoro 1974).

### Flame-Resistant Textiles

Textile products can be made flame resistant by using fibers that are inherently flame resistant or by application of a flame-resistant finish. Modacrylic fibers offer adequate flame resistance at a moderate cost and have some use in carpets, curtains, and children's sleepwear. Many other synthetic fibers shrink from ignition flames, providing some protection. Untreated polyester and nylon, for example, will pass the test for children's sleepwear based on this characteristic.

The more thermally stable materials such as asbestos, glass fiber, the aramids, PBI, and PBO could be called fireproof substances that will not burn. Glass fiber has many industrial uses and may be used to a limited extent in household textile products such as window shades or lamp shades. Thermally stable synthetic fibers have not been developed for general use but rather are intended for specialized protective clothing for industrial and military uses. Not only are they expensive, but they also lack the aesthetic features that would make them useful in consumer products.

For fibers that are not flame resistant, a flame-retardant treatment can be applied. Durable finishes for cotton and cotton blend fabrics contain phosphorus which reacts chemically with the fibers and inhibits the production of compounds that fuel the flame. Commercial flame-retardant finishes are Pyrovatex, Proban, and Py-ron, the latter produced by Ciba Chemicals.

Finishes for synthetic fibers have bromine that quenches the flame by reducing the generation of flammable gases. Tri-2, 3-dibromopropyl phosphate (TRIS) was used for several years to impart flame resistance to nylon and polyester, but was suspected of causing cancer in laboratory animals. Since its removal from the market, and modifications in the test procedure for children's sleepwear, nylon and polyester are not usually finished with a flame-retardant treatment.

A particular problem in textile flammability is the burning of cotton/polyester blends. Since polyester is less flammable than

cotton, one would expect blended fabrics to be less hazardous than all cotton fabrics. This is unfortunately not the case, because the char left as the cotton burns serves to hold the melting and dripping poly-ester in the flame. This is referred to as a "scaffolding" effect that prevents the polyester from dripping away, as it would do in a 100 percent polyester fabric. The polyester remains in the flame and contributes to the burning.

Wool is inherently moderately resistant to burning and provides some protection in apparel and interior furnishings. For more stringent uses such as airplane seats, however, wool is given a flame-retardant treatment. A common finish for wool is Zirpro. performance standards that materials are required to meet are set forth in the CFR. These tests described above usually have a single pass/fail criterion. A wide variety of additional tests for flammability can be conducted to provide information on burning behavior and effectiveness of finishes.

Many of these methods require test samples of considerable size or even whole garments. DuPont, Eastman Kodak, and the University of Minnesota have developed thermal testing manikins with heat sensors located in various parts of the figure. Tests performed using these figures can determine not only the combustibility of the fabric being tested but also the location of hot spots and can furnish data about the transfer of heat. They can also assess effects of fabric layers such as a cotton dress worn over a nylon slip.

There are tests for carpets other than the pill test required by the federal standard. The Flooring Radiant Panel Test is said to simulate conditions of interior fires more effectively than other carpet tests. As a result, it is likely to be used by governmental and other regulatory agencies that require the more extensive product evaluation that carpeting installed in hospitals and facilities participating in Medicare and Medicaid programs must meet.

An area of considerable interest in flammability testing of interiors is computer simulation or virtual tests to determine the hazards of real-life situations. For example, data on the furnishings in a prototype room can be used to predict the results of a fire (Gorman 1994). More realistic measures of fire hazards can be obtained and used in such predictive models. These measures, including total heat release, rate of heat release, and toxic gases evolved, are the real dangers from fires involving textiles.

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resin holds yarns together at the points where the yarns interlace. Resin anti slip fin-ishes are durable.

Other anti-slip finishes can be created by coating silica compounds on fabrics. However, these finishes are only temporary. Temperature-Regulating Finishes

Temperature-regulating fabrics are sensitive to the surrounding temperature or to body heat. Finishes that provide this adaptation include substances called phase change materials (PCMs) (Lennox-Kerr 1998). These substances change from solid to liquid or liquid to solid depending on the temperature. The example we are probably most familiar with is ice changing to water when the temperature rises and then changing back to ice again when cooled. Ice absorbs heat to melt and water gives off heat when it becomes solid. PCMs work the same way but are selected to undergo this phase change around normal skin temperature.

One such finish is polyethylene glycol (PEG), which is applied to fabrics along with a methylol agent such as DMDHEU. The result is a network polymer that is in-solubilized on the surface of the fibers. The polymer absorbs and holds heat energy at high temperature, and then releases the stored energy under cooler conditions. The finish is durable to wear and laundering, because it is cross linked on the fabric.

Not only do these finishes help to warm or cool the body, but they also increase the moisture absorbency of fabrics, thereby further enhancing comfort. Other improved properties are resistance to static, wrinkling, abrasion, pilling, and soil. The PEG finish has been used on T-shirts, underwear, socks, activewear, and biomedical products.

In another form, PCMs have been applied to fabrics as microcapsules in coat-ings, used in nonwoven bonding materials, or included in spinning solutions of man-ufactured fibers. Outlast Technologies, Inc. produces the microcapsules.

Acordis Fibers has produced a version of their Courtelle acrylic fibers with the PCM em-bedded in them. The fabrics made with these fibers are targeted for outdoor apparel, particularly for cold climates. PCM-containing textile fabrics are expensive because the encapsulation process is technology intensive.

### Heat-Reflectant Finishes

An increased level of insulation can be provided in garments and draperies by the ad-dition of heat-reflectant finishes. Most of these products are treated with a spray coat-ing of metal and resinous substances. The heat-reflectant material is sprayed onto the surface of a closely woven fabric. The finish is designed to keep heat either on one side or the other side of the fabric. The finish is effective only with radiated heat.

Lining fabrics are usually constructed so that the finish is applied to the inside of the fabric. The finish reflects the body heat back toward the wearer, thus providing added warmth. In protective clothing to be worn under hot conditions, the finish is worn to the outside to deflect heat away from the body. Draperies may also be treated to provide greater insulation for homes. Treated draperies placed inside windows may serve to keep heat inside the home or to reflect heat outward, preventing it from warming the house.

Some of the processes designed to produce heat reflectance use aluminum in the finish, because it provides excellent reflectancy. A variant of this principle is utilized in fabrics coated or laminated with a thin layer of aluminum, foams, resins, or syn-thetic rubber.

### Light-Reflectant Finishes

Light-reflectant finishes are created by the application of microscopic reflective beads to the surface of a fabric. The increased number of persons who jog or ride bicycles after dark is probably responsible for the application of this finish to a va-riety of garments for sports and to other items such as backpacks. A reflective fin-ish called Scotchlite is produced by the 3M Company. The manufacturer notes that the finish does not alter the color or appearance of the garment by day, but af-ter dark the fabric "lights up" when directly in the path of the lights of an oncom-ing vehicle.

### Light-Resistant Finishes

Many textile fabrics are deteriorated by exposure to sunlight, so attempts have been made to protect fabrics from light damage. Of all the types of rays in the sun's spec-trum, ultraviolet rays are the most destructive of fibers. Although anti-light finishes have yet to be perfected, those that are being tried either coat the fabric or impreg-nate the fibers with materials that absorb ultraviolet rays but are not themselves dam-aged by or removed by exposure to these rays. Such finishes are particularly impor-tant in olefin fabrics, which are degraded by sunlight unless ultraviolet stabilizers are added. Such additives to olefin fibers are permanent and are not lost during usage. Synthetics that have been delustered with titanium dioxide are especially subject to damage from sunlight. This chemical apparently accelerates damage to the fiber and fading of dyes. The addition of certain chemical salts to the melt solution before spinning can ameliorate this problem.

The relationship between exposure to the ultraviolet light of the sun and skin can-cer is well known. Many people assume that fabrics prevent exposure to any part of the body that is covered; however, research shows that fabrics do allow passage of ultraviolet light. Knitted fabrics, which usually have a more open structure, generally allow more ultraviolet light through than woven fabrics; lightweight summer fabrics allow more ultraviolet light to reach the skin than heavier fabrics with more opaque yarns.

Ultraviolet protection is now being built into fibers and fabrics. Most of the techniques are proprietary processes, so details of how the protection is provided are limited. Kuraray, a Japanese firm, produces Esmo, a polyester staple fiber to which powdered ceramics have been added to absorb and reflect ultraviolet rays. A similar fiber called Aloft is produced



by the Japanese firm Toray, and other Japanese firms produce fabrics that are given special protective finishes. Australian researchers have developed a chemical finish called Rayosun that is said to be washfast, colorfast, and lightfast. The finishing material contains a "two-part molecule," one part of which absorbs ultraviolet rays while the other part reacts with the fabric, thereby making the finish durable (Sun-proof clothing 1993, 72).

### Other Specialty Finishes

Several additional finishes produce special effects. In one, a powdered material is applied to fabrics to decrease the loss of body heat. In another, the finishing material contains microencapsulated fragrances that gradually release perfumed oils as the fabric is abraded during wear. The scented finishes have been used in fabrics for men's suits. New, too, are finishes for odor control. These compounds entrap the volatile molecules that cause unpleasant odors.

The preparation steps for fabrics are highly dependent on the fiber content. Natural fibers have impurities such as grease and vegetable matter in wool, gum in silk, or vegetable matter and waxes in cotton. Optimum conditions for spinning fibers into yarns, however, require some lubrication of fibers. Also, in synthetic fibers some means must be found to decrease the static electricity that builds up during spinning. For these reasons, natural lubricating substances in cotton are not removed before spinning, and other fibers generally have had

### Notes



## Durable flame retardant finishing of the nylon/cotton blend fabric using a hydroxyl-functional organophosphorus oligomer

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### Abstract

Cotton/nylon blends have been commonly used as the material for protective clothing, but those blend fabrics are not flame retardant finished because of the unavailability of effective flame retardant finishing systems. Previously, we investigated the use of a hydroxyl-functional flame retardant organophosphorus oligomer (FR) in combination with the mixture of dimethyloldihydroxyethyleneurea (DMDHEU) and trimethylolmelamine (TMM) as the binders for flame retardant finishing of cotton. In this study, we investigated the application of FR to the 50/50 cotton/nylon fabric. When the FR/DMDHEU/TMM system is applied to the fabrics of nylon-6,6 and nylon-6, approximately 40% of the FR applied is permanently bound to the nylon fabrics. FR is bound to the nylon fabrics mainly through the formation of a FR/TMM crosslinked polymeric network, thus becoming durable to multiple launderings. The cotton/nylon blend treated with FR shows high levels of flame retardant performance and excellent laundering durability. The treated fabric passes the vertical flammability test even after 50 home laundering cycles. The fabric stiffness as a result of the finishing process is still an obstacle to be overcome for practical use of this finishing system.  
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**Keywords:** Cotton; Dimethyloldihydroxyethyleneurea; Durable flame retardant finishing; Nylon-6; Nylon-6,6; Nylon/cotton blend; Melamine-formaldehyde; Organophosphorus chemicals

### 1. Introduction

It is difficult to impart durable flame retardancy to nylon fabrics due to low reactivity of nylon and poor penetration of a finishing solution into the fibers. Although aramid fibers, such as Nomex and Kevlar, are inherently flame resistant, the high cost of those aramid fibers has limited their wide applications. In recent years, flame retardant finishing of nylon and nylon/cotton blend fabrics has drawn more and more attention because those fabrics are widely used to

produce protective clothing for military as well as civilian uses.

Several review articles on flame retardant nylon have been published [1–5]. Flame retardant nylon fibers can be produced at the fiber spinning stage using flame retardant additives including organophosphorus and halogenated aliphatic/aromatic compounds [1–4]. However, the high level of the additives required to achieve the flame retardancy may cause significant strength loss of the fiber, and technical difficulties are often encountered during the spinning procedure [1,3]. The second approach is flame retardant finishing of nylon fabrics using a pad-dry-cure process. A number of flame retardant finishing systems, such as thiourea derivatives, ammonium sulfamate and organophosphorus compounds, have been reported as the flame retardant treatment for nylon fabrics using this method [4–10].

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However, none of those technologies has achieved any substantial commercial success.

The flame retardant finishing of a blend fabric containing cotton and a thermoplastic synthetic fiber is difficult because of the "scaffolding effect" of the blend [2,3]. A number of patents have disclosed the use of phosphorus-containing flame retardant agent including the tetrakis(hydroxymethyl)-phosphonium (THP) and urea precondensate to treat cotton/nylon blend, but those flame retardant finishing systems have not been commercialized [11–16]. The nylon/cotton (50/50) blend twill fabric, known as Battledress Uniform (BDU) fabric used to make military uniforms in the U.S., is currently not flame retardant finished due to the unavailability of effective flame retardant finishing technologies.

In our previous study, we used the hydroxyl-functional organophosphorus oligomer with the commercial name of "Fyroltex HP" shown in Scheme 1 (CAS Register No. 70715-06-9, abbreviated as "FR" here) as a flame retardant finishing agent for cotton fabrics when DMDHEU, TMM or multifunctional carboxylic acids were used as the binders [17–21]. The cotton fabric treated with the finishing solution containing FR, DMDHEU and TMM showed excellent flame retardant performance even after 50 home laundering cycles [19,20]. In those finishing systems, both DMDHEU and TMM function as the binders between FR and cotton cellulose and also as the nitrogen providers to enhance the flame retarding performance of FR due to phosphorus–nitrogen synergism [19–21].

In this study, we investigated the bonding of FR to the nylon fabrics as well as to the cotton/nylon blend fabric. We evaluated the flame retardant performance and laundering durability of the cotton/nylon BDU fabric treated with FR in combination with a bonding system.

## 2. Experimental

### 2.1. Materials

Three fabrics were used in this study: (1) 100% nylon-6 knit fabric (Testfabrics Style 304) weighing 73 g/m<sup>2</sup>; (2) 100% nylon-6,6 woven fabric (Testfabrics Style 306A) weighing 59 g/m<sup>2</sup>; and (3) 50/50 nylon/cotton BFU printed fabric weighing 216 g/m<sup>2</sup>. FR ("Fyroltex HP") was a commercial product with nearly 100% active

ingredient supplied by Akzo Nobel Phosphorus Chemical Division, Dobbs Ferry, New York. DMDHEU was a commercial product (44% solid content) with the trade name of "Freerex 900" supplied by Noveon, Cleveland, Ohio. Two melamine–formaldehyde resins were used in this study: (1) TMM, a commercial product (80% solid content) with the trade names of "Aerotex M-3" and (2) XMM, a commercial product of melamine–formaldehyde having the functionality of 4–5 (85% solid content) with the trade name of "Aerotex 3730". Those two melamine–formaldehyde resins were supplied by Noveon, Cleveland, Ohio. The catalyst was an NH<sub>4</sub>Cl-based commercial product with the trade name of "Catalyst RD" supplied by Eastern Color & Chemical, Greenville, South Carolina.

### 2.2. Fabric treatment and home laundering procedures

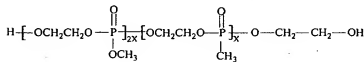
The fabric was first immersed in a finish solution containing FR, the binding agents and the catalyst, then passed through a laboratory padder with two dips and two nips, dried at 90 °C for 3 min, and finally cured in a Mathis curing oven at a specified temperature. All concentrations presented in this study were based on weight of bath (w/w, %) and concentrations of FR, DMDHEU and TMM in all solutions are based on the solid of the chemicals in those chemical products. The wet pick-up of the cotton/nylon fabric was approximately 75%. The wet pick-up of the nylon-6,6 woven fabric and the nylon-6 knit fabric were approximately 60% and 150%, respectively. After curing, the treated fabric was subjected to a specified number of home laundering washing/drying cycles with the use of "AATCC Standard Detergent 1993". The home laundering washing/drying process was done according to AATCC Test Method 124-1996 ("Appearance of Fabrics After Repeated Home Laundering"). The water temperature of laundering was approximately 46 °C.

### 2.3. Evaluation of the flame retarding performance of the fabrics

The vertical flammability of the cotton fabric is measured according to ASTM Standard Method D6413-99. The limiting oxygen index (LOI) of the cotton fabric is measured according to ASTM Standard Method D2863-97.

### 2.4. Determination of phosphorus concentration on the treated fabric

Approximately 2 g of the treated fabric sample taken from three different parts of a "10 × 12" fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. Two milliliters of



Scheme 1. The hydroxy-functional organophosphorus oligomer (FR).

concentrated  $\text{H}_2\text{SO}_4$  were added to 0.1 g of the powder in a beaker. Ten milliliters of 30%  $\text{H}_2\text{O}_2$  were added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250 °C to digest the powder and to evaporate the water until dense  $\text{SO}_3$  vapor was produced. The completely digested sample as a clear solution was transferred to a 50 ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the percent concentration of phosphorus. The percent phosphorus retention is calculated by dividing the phosphorus content of the fabric after laundering by that of the fabric before laundering.

### 2.5. Thermal analysis

Thermogravimetric (TG) experiments were carried out using a Mettler Toledo TGA 851 thermogravimetric analyzer. Samples weight is in the range of 6–8 mg. All samples for TGA were measured from 50 °C to 800 °C at the heating rate 10 °C/min with a continuous air flow. Differential scanning calorimetry (DSC) was measured using a Mettler Toledo DSC 821 analyzer. Aluminum sample holders were used. All samples for DSC were measured from 50 °C to 650 °C at the heating rate of 10 °C/min with a continuous air flow.

## 3. Results and discussion

The nylon-6,6 fabric was treated with 40% FR in combination with 2.6% DMDHEU and 4.8% TMM, dried at 90 °C for 3 min, finally cured at 165 °C for 2 min. The fabric thus treated was subjected to three home laundering cycles. The phosphorus concentration on the treated nylon fabric before laundering was 3.63%, and it became 1.52% after one laundering cycle and remained statistically unchanged after three home laundering cycles (Table 1). One observes that 41% of the FR applied to the nylon-6,6 fabric remained on the fabric after three home laundering cycles.

Table 1

Phosphorus content (%) and percent phosphorus retention of the nylon-6,6 fabric treated with 40% FR, 2.6% DMDHEU and 4.8% TMM, cured at 165 °C for 2 min and subjected to different number of laundering cycles

Number of laundering cycles	Phosphorus concentration (%)	Phosphorus retention (%)
0 <sup>a</sup>	3.63	—
1	1.52	42
3	1.50	41

<sup>a</sup> Before laundering.

Table 2

Phosphorus content (%) and phosphorus retention of the nylon-6 fabric treated with 40% FR, 2.6% DMDHEU and 4.8% TMM, cured at 165 °C for 2 min and subjected to different number of laundering cycles

Number of laundering cycles	Phosphorus concentration (%)	Phosphorus retention (%)
0	6.51	—
1	2.72	42
3	2.72	42

The nylon-6 fabric was also treated with the same finishing solution and cured at 165 °C for 2 min. The amount of FR applied to the nylon-6 fabric was significantly higher than that applied to the nylon-6,6 fabric as a result of the drastically higher wet pick-up due to the loose structure and higher absorbency of the knit fabric. The initial phosphorus concentration on the treated nylon fabric before laundering was 6.51% (Table 2). After the treated nylon-6 fabric was subjected to three home laundering cycles, however, the percent retention of phosphorus on the nylon-6 fabric (42%) was very close to that on the treated nylon-6,6 fabric (41%). It should also be pointed out that the amount of phosphorus on the treated nylon fabrics shows almost no reduction as the number of home laundering cycles increased from one to three (Tables 1 and 2). Thus, the data presented here clearly indicate that the flame retardant organophosphorus oligomer bound to the nylon fabrics was durable to multiple home laundering cycles.

Thermal analysis techniques (TG, DTG and DSC) were used to study the nylon-6,6 and nylon-6 fabrics treated with the finishing solution containing FR/DMDHEU/TMM described above. The TG, DTG and DCS curves of the treated nylon-6,6 fabric measured in air atmosphere are presented in Figs. 1, 2 and 3, respectively. The untreated nylon-6,6 fabric started to lose weight at 360 °C (Fig. 1). The rate of weight loss reached its maximum at 412 °C as indicated

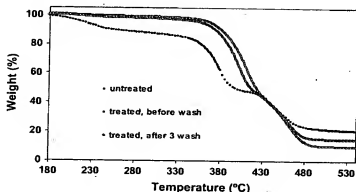


Fig. 1. TG curves of the untreated nylon-6,6 fabric and that treated with 40% FR, 2.6% DMDHEU and 4.8% TMM, and cured at 165 °C for 2 min.

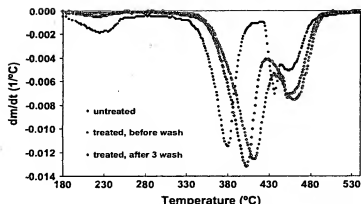


Fig. 2. DTG curves of the untreated nylon-6,6 fabric and that treated with 40% FR, 2.6% DMDHEU and 4.8% TMM, and cured at 165 °C for 2 min.

by the peak in the DTG curve (Fig. 2). The weight loss of the untreated nylon fabric was attributed to the thermal decomposition of nylon-6,6, which caused the main chain breakdown with the formation of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$  and hydrocarbons [22,23]. The decomposition of nylon-6,6 in this temperature range is confirmed by the endothermal peak at 412 °C in the DSC curve of the nylon-6,6 fabric (Fig. 3). The untreated nylon-6,6 lost 90% of its original weight with 10% residual solid at 500 °C (Fig. 1).

After the nylon-6,6 fabric was treated with FR and before it underwent home laundering, the rate of weight loss of the fabric thus treated reached its maximum at 379 °C as a result of the presence of FR on the nylon fabric (Fig. 2), and the DSC curve of the fabric also shows an endothermal peak at 379 °C (Fig. 3). The treated fabric lost 79% of its original weight as the temperature was increased to 500 °C with 21% solid residual (Fig. 1). The data presented indicate that the presence of the organophosphorus oligomer on the nylon fabric lowered the decomposition temperature

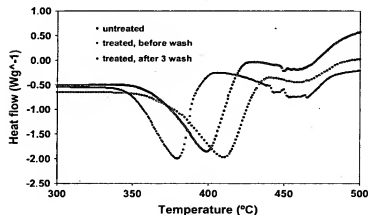


Fig. 3. DSC curves of the untreated nylon-6,6 fabric and that treated with 40% FR, 2.6% DMDHEU and 4.8% TMM, and cured at 165 °C for 2 min.

and enhanced the formation of char after pyrolysis of the fabric sample.

The TG, DTG and DSC curves of the nylon-6,6 fabric treated with FR and subjected to three home laundering cycles are also presented in Figs. 1, 2 and 3, respectively. Both DTG and DSC curves show the decomposition peak at 398 °C, which is notably lower than that of the untreated nylon (412 °C). The TG curve reveals that the nylon-6,6 fabric lost 83% of its original weight at 500 °C with 17% solid residual (Fig. 1). The data presented here clearly suggest that the FR on the treated nylon-6,6 fabric not only lowered the decomposition temperature but also increased quantity of the solid residual after pyrolysis during the TG experiment.

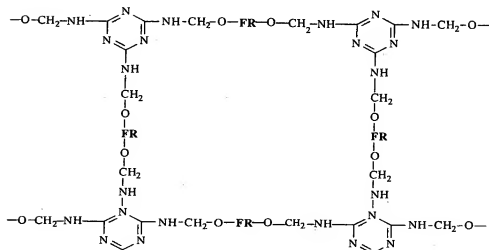
We also studied the effects of the FR-based finishing system on the thermal properties of the nylon-6 fabric using the thermal analysis techniques. The nylon-6 fabric was also treated with the finishing solution containing 40% FR, 2.6% DMDHEU and 4.8% TMM, and cured at 165 °C for 2 min. The TG, DTG and DSC data are summarized in Table 3. One observes similar phenomenon that the decomposition temperature of the treated fabric was reduced and the solid residual after pyrolysis was increased when the nylon-6 fabric was treated with FR/DMDHEU/TMM. Thus, the thermal analysis data of both the treated nylon-6,6 and the treated nylon-6 fabrics demonstrate that the organophosphorus oligomer applied to the nylon fabrics was retained on the fabrics after home laundering.

The fact that more than 40% of the FR applied to the two different nylon fabrics remained on the fabrics after three home laundering cycles demonstrates that the FR applied to the nylon fabric has good laundering durability after the curing process. The bonding of FR to the nylon fiber may be attributed to the reactions of the bonding agents (DMDHEU or TMM) with both FR and terminal amine groups of the nylon fibers. Those bonding agents had multiple hemiacetal groups in their molecules to react with both hydroxyl groups of FR and the terminal amine groups of the nylon fibers, thus forming "bridges" between FR and the nylon fibers. The typical concentration of the terminal amine group of nylon-6,6 is 40  $\mu\text{mole/g}$  [24]. Assuming FR reacts

Table 3

The DTG peaks, DSC peaks and the TG total weight loss of the untreated nylon-6 fabric and the nylon-6 fabric treated with 40% FR, 2.6% DMDHEU and 4.8% TMM and cured at 165 °C for 2 min

Sample description	DTG peak (°C)	DSC endothermal peak (°C)	TG solid residual at 500 °C (%)
Untreated nylon-6 fabric	424	425	10
Treated nylon-6 fabric before laundering	343	342	23
Treated nylon-6 fabric subjected to three laundering cycles	395	397	15



Scheme 2. The FR/TMM polymeric network.

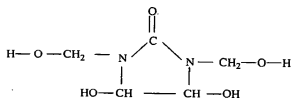
with every terminal amine group in the nylon-6,6 fiber through DMDHEU/TMM and also assuming that  $x = 1$  in Scheme 1, the maximum phosphorus concentration on the nylon-6,6 fiber is 0.23% (w/w). Considering the facts that the penetration of FR into the nylon fiber is poor and that the efficiency of bonding FR to cotton cellulose is approximately 60% when DMDHEU or TMM are used as the binders, the concentration of the phosphorus bound to the nylon fiber through the terminal amine groups should be far less than the maximum value of 0.23%. The data presented above show that the initial phosphorus concentration before wash on the nylon-6 fabric (4.51%) was 1.8 times that on the nylon-6,6 fabric (3.63%). The percent phosphorus retention after three laundering cycles remained the same (41%–42%) for those two fabrics. Therefore, the amount of FR bound to the nylon fabrics through the terminal amine groups of nylon is probably insignificant. We can conclude that the laundering durability of the FR on the nylon fabrics is mainly attributed to the formation of crosslinked polymeric network shown in Scheme 2. FR on the nylon fibers became a part of the crosslinked polymeric network, thus becoming durable to multiple laundering cycles.

In our previous research, we also found that the two hemiacetal groups originated from glyoxal in a DMDHEU molecule (Scheme 3) are far less reactive than those of formaldehyde. Consequently, DMDHEU

mainly functions as a bifunctional reagent and reacts with FR to form a linear condensation product.

The cotton/nylon BDU fabric was treated with 40% FR in combination with DMDHEU/TMM and with XMM/TMM, as shown in Table 4, and cured at 165 °C for 2 min. The fabric thus treated was subjected to different numbers of home laundering cycles. The phosphorus concentration and the percent phosphorus retention of the treated fabric are shown in Table 5 and Fig. 4, respectively. The phosphorus concentrations (before laundering) on the fabric treated with FR/DMDHEU/TMM and FR/XMM/TMM were 3.93% and 3.89%, respectively. It decreased to 2.47% and 2.18% for the fabric treated with FR/XMM/TMM and FR/DMDHEU/TMM, respectively, after one laundering cycle, which represented 63% and 55% retention of FR on the fabric (Fig. 4). As the number of laundering cycle increased to 40, the phosphorus retention decreased to 36% and 25% for the fabric treated using XMM/TMM and DMDHEU/TMM as the binders, respectively (Fig. 4). Thus, the data presented here demonstrate that the phosphorus retention of the fabric treated with FR/XMM/TMM is notably higher than that treated with FR/DMDHEU/TMM, and the difference became more significant as the number of laundering cycle increased.

The two formulas contained the same concentration of FR and TMM. The only difference was the second



Scheme 3. DMDHEU.

Table 4

The formulas (A1–A2) used for the treatment of cotton/nylon blend fabric

Sample code	FR (%)	DMDHEU (%)	XMM (%)	TMM (%)	Catalyst (%)	Wetting agent (%)	Wet pick-up (%)
A1	40	3.5	—	4.8	0.2	0.2	78
A2	40	—	3.4	4.8	0.2	0.2	80

Table 5

The phosphorus concentration (%) of the cotton/nylon blend (50/50) treated 40% FR and different binders, and cured at 165 °C for 2 min

Sample code	Binding system	Number of home laundering cycles				
		0	1	10	20	40
A1	3.5% DMDHEU	3.93	2.18	1.59	1.18	0.97
	4.8% TMM					
A2	3.4% XMM	3.89	2.47	1.99	1.65	1.39
	4.8% TMM					

bonding agent in the formulas. The fabric treated with DMDHEU/TMM as the binders showed significantly lower phosphorus retention throughout the 40 laundering cycles than that treated with XMM/TMM (Fig. 4). Thus, the data presented clearly indicate that XMM is a more effective bonding agent for FR on the cotton/nylon blend, and the FR bound to the fabric using XMM/TMM as the bonding agents is more durable to home laundering than that using DMDHEU/TMM.

The different effectiveness as a binder between XMM and DMDHEU was probably related to their ability to form a crosslinked polymeric network with FR on the fabric. Since XMM has a higher functionality than TMM, it has higher reactivity towards FR to form a crosslinked network than TMM. The higher laundering durability of the fabric treated using XMM/TMM as the binders can be attributed to the increased amount of the crosslinked network formed on the fabric. DMDHEU, on the other hand, forms linear structures with FR, as discussed previously. We found that the fabric treated with XMM/TMM showed higher stiffness than that treated with DMDHEU/TMM, which was an indication that the amount of the crosslinked network was increased on the cotton/nylon blend as the DMDHEU was replaced by XMM in the formula. The change of nylon fabric stiffness with different bonding agents in the flame retardant finishing systems will be discussed in a subsequent paper.

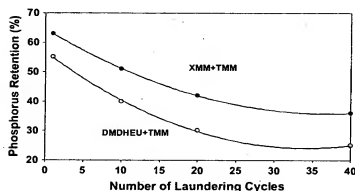


Fig. 4. The percent phosphorus retention of the nylon/cotton (50/50) blend fabric treated with 40% FR in combination with DMDHEU/TMM and XMM/TMM as a function of the number of home laundering cycles.

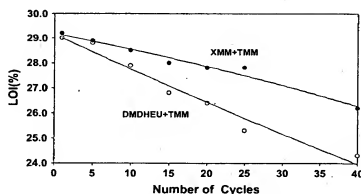


Fig. 5. The LOI (%) of the nylon/cotton (50/50) blend fabric treated with 40% FR in combination with DMDHEU/TMM and with TMM/XMM as a function of the number of home laundering cycles.

The LOI (%) of the cotton/nylon fabric treated with the two formulas is plotted against the number of laundering cycles in Fig. 5. One observes that as the number of laundering cycle increased, the LOI of the fabric treated with XMM/TMM became significantly higher than that treated with DMDHEU/TMM (Fig. 5), thus conforming that the fabric treated with XMM/TMM had higher laundering durability than that treated with DMDHEU/TMM. The difference in LOI between those two treated fabric samples became more overwhelming as the number of laundering cycle increased (Fig. 4).

We also investigated the performance of the FR-based flame retardant finishing system using different concentrations of FR, TMM and XMM, two different formulas containing FR at two concentration levels (32% and 40%), 3.4% XMM, and TMM at two concentration levels (5.1% and 2.6%) (Table 6). The treated fabric samples were cured at 165 °C for 2 min. The phosphorus concentration on the fabric treated with 40% FR, 3.4% XMM and 2.6% TMM (Sample B1) is compared with that treated with 32% FR, 3.4% XMM and 5.1% TMM (Sample B2) in Table 7, and the percent phosphorus retention of the fabric samples thus treated is plotted against the number of home laundering cycles in Fig. 5. The initial phosphorus concentration for fabric Sample B1 (3.79%) was significantly higher than that of Sample B2 (3.09%), because Sample B1 was treated with 40% FR whereas Sample B2 was treated with 32% FR (Table 6). After one laundering

Table 6

The formulas (B1–B2) used for the treatment of cotton/nylon blend fabric

Sample code	FR (%)	XMM (%)	TMM (%)	Catalyst (%)	Wetting agent (%)	Wet pick-up (%)
B1	40	3.4	2.6	0.2	0.2	78
B2	32	3.4	5.1	0.2	0.2	77

Table 7

The phosphorus concentration (%) of the cotton/nylon blend treated with the formulas B1–B2 and cured at 165 °C for 2 min

Sample FR concentration		Number of home laundering cycles					
code	(%)	0	1	10	20	40	50
B1	40	3.79	2.26	1.15	1.28	0.96	—
B2	32	3.09	2.17	1.91	1.89	1.50	1.43

cycle, Sample B2 showed higher phosphorus retention (70%) than that of Sample B1 (60%) even though its phosphorus concentration (2.17%) is slightly lower than that of Sample B1 (2.26%). When the number of the home launderings increased to 10, the phosphorus concentration of Sample B2 (1.91%) becomes notably higher than that of Sample B1 (1.55%) with corresponding phosphorus retention at 62% and 41%. The difference in percent phosphorus retention for the two treated fabric samples became more profound as the number of laundering cycle increased further. After 20 laundering cycles, Sample B2 showed 61% retention of the applied FR whereas Sample B1 had only 34% retention (Fig. 6). Thus, the data indicate that the combination of 3.4% XMM and 5.1% TMM as the binders in the system provided significantly higher retention of the FR on the fabric and also improved laundering durability.

The LOI and char length of the two treated fabric samples are presented in Tables 8 and 9, respectively. Fabric Sample B2 had LOI (29.5%) slightly higher than that of Sample B1 (29.3%) before wash even though its phosphorus content (3.09%) was lower than that of Sample B1 (3.79%). This was because the TMM concentration for Sample B2 (5.1%) is significantly higher than that of Sample B1 (2.6%). Since TMM functions as a nitrogen provider to enhance the flame retarding performance by means of phosphorus–nitrogen synergism [18–20], a higher TMM concentration in formula B2 raised the LOI of the treated fabric sample.

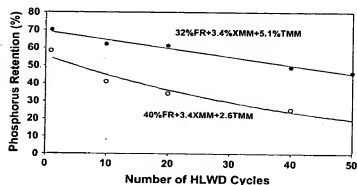


Fig. 6. The percent phosphorus retention of the nylon/cotton (50/50) blend fabric treated with FR and different melamine–formaldehyde bonding agents as a function of the number of home laundering cycles.

Table 8

The LOI (%) of the cotton/nylon blend treated with the formulas B1–B2 and cured at 165 °C for 2 min

Sample FR concentration		Number of home laundering cycles					
code	(%)	0	1	10	20	40	50
B1	40	29.3	28.4	27.2	26.1	24.5	—
B2	32	29.5	28.6	28.0	28.1	26.9	26.0

During the entire 50 home laundering cycles, Sample B2 maintained higher LOI than Sample B1, as shown in Table 8, in spite of the lower FR concentration in its formula. Fabric Sample B2 passed the vertical flammability test with a char length of 9.6 cm after 50 laundering cycles whereas Sample B1 failed the test after 40 laundering cycles (Table 9). Therefore, the fabric treated with 32% FR, 3.4% XMM and 5.1% TMM demonstrated notably better flame retarding performance and laundering durability than that treated with 40% FR, 3.4% XMM and 2.6% TMM.

In our previous research on the FR/TMM system, we found that the formation of a crosslinked network takes place only in certain FR/TMM weight ratio range [20]. The higher retention of the flame retarding agent on fabric and the better flame retarding performance after multiple laundering cycles for the fabric with a lower concentration of FR and higher concentration of the binding agents indicate that the FR-to-binder ratio in a formula plays a critical role in determining the performance of this flame retarding system.

#### 4. Conclusions

The FR applied to the nylon-6,6 and nylon-6 fabrics becomes durable to home laundering when a bonding system including DMDHEU and TMM is present. The laundering durability of FR is probably attributed to the formation of a FR/TMM crosslinked polymeric network on the nylon fabrics.

The cotton/nylon BDU fabric treated with the combination of TMM and XMM shows high levels of flame retarding performance and laundering durability. The selection of the binders and the binders-to-FR weight ratio in a finish formulation are the two most critical parameters for achieving higher levels of flame retarding performance.

Table 9

The char length (cm) of the cotton/nylon blend treated with formulas B1–B2 and cured at 165 °C for 2 min

Sample FR concentration		Number of home laundering cycles					
code	(%)	0	1	10	20	40	50
B1	40	5.0	8.4	7.8	5.8	>30	>30
B2	32	5.8	6.5	9.3	6.8	8.2	9.6



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# Production of Flame-Retardant Nylon 6 and 6.6

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1. INTRODUCTION .....	85
2. THERMAL BEHAVIOR OF NYLON 6 AND 6.6 .....	86
3. FLAMMABILITY CHARACTERISTICS OF NYLON 6 AND 6.6 .....	87
4. FLAME-RETARDANT NYLON 6 AND 6.6 .....	88
4.1. Flame-Retardant Mechanism .....	88
4.2. Production of Flame-Retardant Nylon Fibers .....	90
4.3. Manufacture of Flame-Retardant Nylon Plastics .....	97
5. SUMMARY .....	100
REFERENCES .....	101

## 1. INTRODUCTION

Flame-retardant textiles are important constituents of various protective clothing, particularly for defense applications like clothing for nuclear-biological-chemical warfare, tank crew overalls, tarpaulins, camouflage nets, ballistic and thermal protection wear and also for industrial applications such as thermal protection wear for firefighters, welder's clothing, and for industries having a high risk of fire hazards. These textiles are

also used as tapestry, curtains, and upholstery in hospitals, hotels, and the like. In the United States, even sleepwear needs to be flame retardant.

Every textile fiber type burns differently, and during the burning process, the textile fiber thermally decomposes. This produces different products, including some toxic gases. These toxic gases evolve either from the basic textile substrate or from the flame-retardant chemicals used in the textiles. The casualties during fire are mostly due to inhalation of toxic gases developed during the burning process of the textiles. Many studies have shown that 50–60% of the victims succumbing at a fire die from inhaling smoke and toxic gases and not from direct fire or burns [1]. Therefore, the toxicology of flame-retardant materials must be given more consideration to minimize the hazards, while selecting a suitable flame retardant for any textile. In most of the studies, factors other than flammability have been almost neglected. Therefore, the carcinogenicity and mutagenicity of flame retardants and their possible effects on the environment need to be tested. Toxicity of any burning material is evaluated by measuring the lethality of a material burned under specified combustion conditions, with the test animals inhaling the smoke for a fixed time period. Computer models now exist for rigorous calculation of fire hazards [2].

Generally, polyamides show better resistance to wear and abrasion, low coefficient of friction, good resilience, and high impact strength. Nylon 6 has better thermal and weather resistance in comparison to nylon 6.6; however, nylon 6.6 has higher rigidity than nylon 6. Apart from the above two nylons, other commercially available polyamide fibers include nylon 6.10, nylon 11, nylon 12, nylon 4.6, and aromatic polyamides such as Nomex and Kevlar. Nylon 11 and nylon 12 have been used in the manufacture of electrical insulators, battery casings for aircraft use, and gear wheels for water meters. Nylon 6 and nylon 6.6 represent more than 98% of the total polyamide volume; practically, these two polyamides are used interchangeably in most applications [3, 4]. The aromatic polyamides are essentially used for high-temperature applications like thermal protective clothing, firefighter suits, and some other industrial applications.

Many research papers have appeared in the literature; however, no exhaustive review exists on flame-retardant polyamides. In the present paper, we review the work carried out by various researchers for nylon 6 and nylon 6.6, which are commercially popular fibers.

## 2. THERMAL BEHAVIOR OF NYLON 6 AND 6.6

To select the appropriate flame-retarding agents for nylon 6 and 6.6, it is necessary to understand their thermal behavior. Generally, when the polymeric materials are burned, the gases evolved are CO, NO<sub>2</sub>, HCN, and the like, which are toxic [5]. When different fibers are subjected to the International Organization for Standardization (ISO) "N" gas model test, which is a bench-scale test for toxic potency, it is observed that the evolution of CO differs from fiber to fiber. Among the natural fibers, evolution of CO is greater from cotton than wool. Among the synthetic fibers, the evolution of CO from nylon 6.6 is next only to that from polypropylene. The following important fibers are arranged in decreasing order for the evolution of CO [6]:

Cotton > Polypropylene > Nylon 6.6 > Polyurethane > Polyvinyl Chloride > Wool

Textile fibers can be divided into two classes based on their relative ignitability [7]: (1) fibers that char when ignited, such as viscose, cotton, wool, and the like; and (2)

fibers that melt when ignited, such as polyamides, polyesters, polypropylene, and so on. The chemical composition, bond energies, and intermolecular cohesive forces are some of the factors affecting the flammability of any organic polymer [8-10]. The decomposition of cellulosic material produces levoglucosan and char. As the reaction continues, this levoglucosan further decomposes into large amounts of flammable volatile products that propagate the flame and small amounts of carbonaceous char. In contrast, polyamides, polyester, and the like, being thermoplastic, melt and decompose on ignition. The dripping molten polymer adheres to the skin and greatly aggravates burn injuries of the wearer.

Burning characteristics of various synthetic and natural fibers are given in Table 1. Nylon 6 and nylon 6.6 both soften at 50°C and melt at 215°C and 265°C, respectively. Nylon 6 pyrolyzes above 430°C and undergoes combustion at 450°C. For nylon 6.6, the pyrolysis and combustion temperatures are about 403°C and 530°C, respectively. A pyrolysis temperature is the temperature at which chemical degradation takes place by the action of heat in the absence of air; pyrolysis is the essential first step in the combustion of polymers. The combustion temperature is the temperature at which chemical decomposition takes place by a combination of the substance with oxygen, causing evolution of light and heat during a burning reaction [11, 12]. The limiting oxygen index (LOI) value for the untreated nylon 6 and 6.6 are about 21-22%. The LOI is the minimum percentage of oxygen required in an oxygen-nitrogen mixture to sustain the downward burning of the material. The heat of combustion  $\Delta H$  is 39 kJ/g for nylon 6 and 32 kJ/g for nylon 6.6. The heat of combustion is defined as the energy generated in a flaming combustion process per unit mass of the material vaporized [13].

Among the natural and other conventional synthetic fibers, wool has a maximum combustion temperature of about 600°C and yields higher LOI values (i.e., 25-27%). Acrylics, cotton, and viscose have lower pyrolysis and combustion temperatures, and the LOI value is lower (i.e., around 18-20%). Hence, these fibers catch fire quickly.

### 3. FLAMMABILITY CHARACTERISTICS OF NYLON 6 AND 6.6

Polyamides burn slowly, drip, and may self-extinguish; the difficulty in burning a polyamide is due to the large difference between the melting and ignition points of

TABLE 1  
Thermal Transition Temperatures and Limiting Oxygen Index (LOI) of Some Fibers

Fiber	$T_g$ , °C	$T_m$ , °C	$T_p$ , °C (pyrolysis)	$T_c$ , °C (combustion)	$\Delta H$ , kJg <sup>-1</sup>	LOI, %
Nylon 6	50	215	431	450	39	21-22
Nylon 6.6	50	265	403	530	32	21-22
Polyester	80-90	250-255	400-477	480	24	22
Acrylic	90-100	>320	290	>250	32	19
Cotton	—	—	350	350	19	18-20
Viscose	—	—	350	420	19	18-19
Wool	—	—	245	600	27	25-27

Source: From Refs. 14 and 15.

polyamides coupled with their low melt viscosities [16]. The heat generated during combustion is sufficient to melt the polymer. Nylons also ignite more easily than many natural fibers.

Nylon has self-extinguishing properties due to extensive shrinkage and dripping during combustion [17]. When the nylon polymer is ignited, first it melts, and then the molten droplets drip away from the flame. Quite often, most of the heat is carried away with the droplet, making the material self-extinguishing. However, if the molten droplets burn continuously, this will promote a greater fire hazard.

Although the nylon fiber has self-extinguishing properties, there are serious problems when it is blended with nonthermoplastic fibers owing to the "scaffolding effect" [18-20, 45]. For example, cellulose fibers char, and this carbonaceous char acts as a supporting structure that causes the molten polymer to remain exposed to the flame, and thus the blend burns vigorously.

Nylon 6 has a lower melting point than nylon 6,6, and this may be one of the reasons for the difficulties in rendering flame retardancy to nylon 6 compared to nylon 6,6 [21].

Under vacuum at temperatures above 300°C, the main decomposition products released by polyamides are about 95% nonvolatiles [22-28]. The volatile products mainly consist of CO<sub>2</sub>, CO, water, ethanol, benzene, cyclopentanone, ammonia, numerous other aliphatic and aromatic hydrocarbons, and saturated and unsaturated molecules [29, 30].

However, when polyamides are heated at temperatures below 200°C in the presence of oxygen, the degradation patterns are different [31, 32]. Thermal oxidation shows the volatile products to be as follows: water 52%, CO<sub>2</sub> 33%, CO 12%, and methanol, formaldehyde, and acetaldehyde are around 1% each. Photooxidation and irradiation of low molecular weight polyamide suggest that the most labile hydrogen atom in the polyamide molecule is on the carbon atom adjacent to the -NH group [33-35]. When nylon is pyrolyzed the process causes depolymerization [36].

The suggested oxidative decomposition mechanism for nylon is given in Fig. 1 [37].

Levantovskoeva assumed that, in analogy with the oxidative degradation of hydrocarbons, the oxygen molecule initiates the chain process of oxidation of polyamides (Eq. 1 in Fig. 1). At the point of abstraction of the hydrogen atom, either a peroxide radical or a hydroperoxide is formed (Eqs. 2 and 3, Fig. 1). During the decomposition of hydroperoxide, water is formed (Eq. 4, Fig. 1). The formation of water can lead to the hydrolysis of the polymer that, on decarboxylation, produces CO<sub>2</sub>. In addition to the decomposition of peroxide, breakdown of peroxide radicals may also take place. The peroxide radical may isomerize by the reaction with the free valence of the adjacent C-C bond. Isomerization and breakdown of the peroxide radical result in chain rupture, which in turn forms a molecule with a terminal aldehyde group (a) and a radical (b) (Eq. 5 in Fig. 1). The decomposition of (a) leads to formation of CO (Eq. 6, Fig. 1). Radical (b) can break down with the rupture of the C-C bond and the formation of a second C-O bond, which leads to the production of formaldehyde (Eq. 7, Fig. 1).

#### 4. FLAME-RETARDANT NYLON 6 AND 6,6

##### 4.1. Flame-Retardant Mechanism

Natural fibers and conventional man-made fibers (e.g., polyester, polyamide, acrylic, polypropylene, and rayon) are liable to ignite in different ways, so different

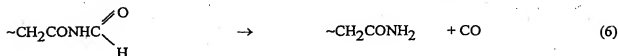
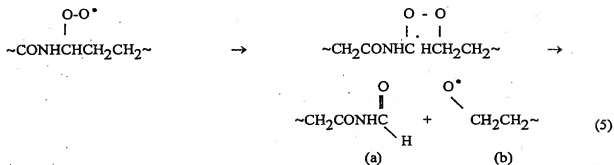
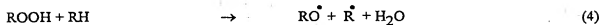
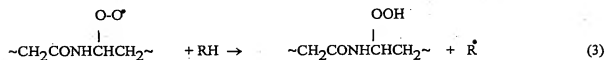
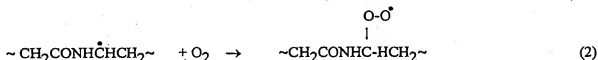
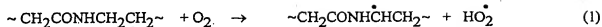


FIG. 1. Suggested oxidative decomposition mechanism for nylons.

flame-retardant mechanisms are found operative in different fibers. Study about the mechanism of action of various flame retardants on textiles is therefore essential to evaluate a particular flame-retardant system. The two mechanisms of flame retardancy are (1) gas/vapor phase mechanism and (2) solid/condensed phase mechanism.

The flame retardant acting in the gas phase mechanism generally does not change the thermal decomposition of a polymer, and the volatile gas output remains virtually the same. In the gas phase mechanism, during the combustion process, the textile material consisting of a flame-retarding agent decomposes into free radicals due to heat. These free radicals combine with atmospheric oxygen/air through complex reactions. Thus, the oxygen then combined is unavailable for the oxidation of flammable gases generated by the decomposition of polymer substrate and hence retards the combustion process [38].

The condensed phase mechanism involves changes in the polymer substrate. Systems that promote extensive polymer cross-linking at the surface form a carbonaceous char on heating. Char insulates the underlying polymer from the heat of the flame, preventing production of new fuel and further burning. Other systems evolve water during

heating, cooling the surface, and increasing the amount of energy needed to maintain the flame [39].

Flame-retardant fibers can be generally classified into two classes [40]: (1) inherently flame retardant fibers, like aramides, PBI (polybenzimidazole), polyamide-imide, and the like; and (2) fibers with chemical structure or surface characteristics that have been chemically modified to make them so.

The first group possesses some entirely new properties; they are called high-performance fibers [41]. The second group retains most of the properties of the unmodified fiber, which could be nylon, polyester, acrylic, viscose, or others. Aramids are used for flame-retardant protective clothing due to their high-temperature resistance and high tenacity. They are also used in composite materials, such as personal armor and vehicle armor against ballistic attack, due to their high strength-to-weight ratio [42]. The flammability profiles of aramid fibers and nylon are depicted in Fig. 2 [43].

#### 4.2. Production of Flame-Retardant Nylon Fibers

Flame-retardant behavior can be rendered to the second group of fibers (i.e., conventional polyester, polyamide, acrylic, etc.) in three different ways [44, 45]: (1) at the polymerization stage using certain phosphorus- and/or halogen-based comonomers in the fiber-forming polymers; (2) by adding flame-retardant additives in the spinning dope/spinning bath before extrusion; (3) surface treatment or topical finishing using flame-retardant finishes. Table 2 gives the various possible ways of rendering fire resistance to conventional synthetic fibers according to the method and the nature of the polymeric substrate [17].

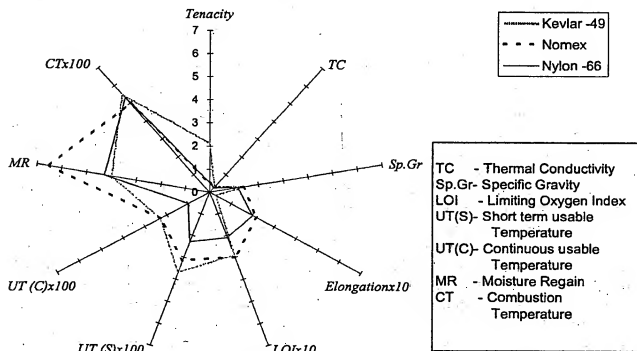


FIG. 2. Flammability profiles.

4.2.1. *Modification During Polymerization*

Synthetic fibers may be made effectively flame retardant by polymer modification, so that the polymer easily drips away from the flame during its exposure to heat. For this purpose, halogenated compounds have been found very effective [46-48]. These compounds operate through the vapor phase mechanism. On heating, the halogenated compounds decompose and give rise to free radicals. These free radicals react with oxygen and prevent the inflammable volatile gases developed during burning of the material from oxidation. Thus, the combustion of burning substrate is retarded. The halogenated compounds exhibit synergistic flame-retardant effects when used with antimony oxide.

The flame-retarding agents used for nylon during the polymerization process are red phosphorus and phosphorus-containing compounds like bis(2-carboxyethyl) methyl phosphine oxide (CEMPO). The major problems when halogenated compounds are used arises from the dehalogenation and dehydrohalogenation reactions that can occur at high temperatures, and they are not stable enough to be held under vacuum at a high temperature for a long time during spinning [49].

It is assumed that the red phosphorus exhibits a vapor phase mechanism of flame retardancy in oxygen-containing polymeric substrates like polyester, polyamides, polyurethane, and the like [50], whereas the condensed phase action of red phosphorus has been proposed for nonoxygenated polymers like polyacrylonitrile [51-53]. Red phosphorus is highly explosive, and its use for flame retardancy as such is dangerous. So, it is mixed with an inert synergist like magnesium hydroxide or aluminum trihydrate. A number of flame-retardant chemicals are used for nylon 6 and nylon 6.6 during the polymerization process (Table 3).

$\epsilon$ -Caprolactam undergoes anionic polymerization in the presence of 5 wt% red phosphorus and 5 wt% magnesium oxide to give flame-retardant nylon 6 with an LOI of 28.5% [49]. The process is initiated by sodium or lithium caprolactamate and activated by *N*-acetyl caprolactam (both 1 mol% on the basis of monomer). The particle size of red phosphorus is less than 40  $\mu$ .

Marik et al. [54] prepared fire-retardant polyamides by the anionic polymerization of 9.5:0.5 caprolactam-laurolactam melt, homogenized with 0.5 mol% toluene diisocyanate (TDI), caprolactam-red phosphorus mixture with 1.5% phosphorus content in the polymer and 0.25 mol% catalyst sodium dicaprolactamo-bis(2-methoxy ethoxy) aluminate and heating at 240°C.

TABLE 2  
Methods of Adding Fire Resistance

Flame retardant method	Polyamide	Polyester	Acrylic
Copolymerization	(+)	++	++
Spinning dope/bath	(+)	+	+
Topical finishing	+	+	(+)

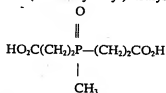
++, important; +, less important; (+), minor importance.



TABLE 3  
Modification During Polymerization

Reagents	Properties	Reference
$\epsilon$ -Caprolactam + 5 wt% Red Phosphorus + 5 wt% MgO $\xrightarrow[\text{Polymerization}]{\text{Anionic}}$ Flame-retardant Nylon 6	LOI 28.5%	49
9.5:0.5 Caprolactam-lauro lactam + 0.5 mol% TDI + Caprolactam Melt-Red Phosphorus (1.5%) Mixture + 0.25 mol% Sodium Dicaprolactam-bis-(2-Methoxy Ethoxy) Aluminate Nylon 66 salt + 30 mol% CEMPO <sup>a</sup> + HMD + Water	FR properties achieved          LOI 25.3%   Tenacity 2.8 gpd Boiling water shrinkage 40% Moisture regain 7% (at 65% RH) Melting point 225°C	54          55

<sup>a</sup>Bis(2-carboxy ethyl)methyl phosphine oxide (CEMPO), mp = 175°C–177°C:



Nylon 6.6 is made flame retardant by melt polymerizing nylon 6.6 salt with 30 mol% CEMPO and hexamethylene diamine (HMD). Water is added to make a total charge of 75% of polymer [55]. The finished polymer is extruded and drawn to approximately 4.5 times over a hot pin at 60°C–90°C, which gives a fiber of LOI 25.3% and melting temperature of 225°C. Fiber properties are not much affected up to 35 mol% of CEMPO.

#### 4.2.2. Modification During Spinning

It is an economical method to incorporate flame-retarding agent in the molten nylon while spinning/extrusion to yield a durable treatment. Most of the phosphorus, metal, and halogen additives, however, are not stable at the fiber-spinning temperature. Moreover, their presence changes the properties of the polymer considerably. Hence, one has to carefully select low molecular weight phosphorus, halogen, and inorganic com-

pounds to balance the benefits of the flame-retarding nylon with the adverse side effects caused by these additives to the polymer property.

Some of the flame-retardant additives used in the spinning dope are low molecular weight phosphorus compounds, chlorinated polyethylene, brominated pentaerythritol, antimony oxide, and so on (Table 4).

Butylkina, Ivanova, and Tyuganova [56] investigated the flammability characteristics of the nylon 6 fiber in the presence of various phosphorus-containing flame-retardant additives such as (i) lead methyl phosphonate, (ii) a complex compound of an alkyl phosphonic acid and antimony, (iii) phosphorylated pentaerythritol (fostertrol), and (iv) the phosphorus-containing compound borofos.

Compounds (i) and (ii) belong to the class of nonmelting compounds and (iii) and (iv) are highly viscous liquids. They suggested that it is advisable to use 25% by weight of borofos or 25% by weight of the complex salt of an alkyl phosphonic acid with antimony since these two compounds markedly reduce the rate of decomposition by causing intensive char formation by the polymer. All four flame-retardant additives are stable at the fiber-spinning temperature. The most marked change in  $T_g$  from 52°C–68°C

TABLE 4  
Modification During Spinning

Reagents	Properties	Reference
(i) Polycapraamide + 25% by wt Borofos (Phosphorus-Containing Compound)	Increase in $T_g$ 52°C–68°C	56
(ii) Polycapraamide + 25% by wt of Complex Compound of an Alkyl Phosphonic Acid and Antimony	LOI 29–30%	
75 parts Nylon 6 + 15.25 parts Chlorinated Polyethylene (25% Cl) + 7.75 parts Kemgard 425 <sup>a</sup> + 2 parts Additives (master batch), 1:11.5 master batch:Nylon 6 melt spun	FR properties achieved	57
Nylon 6 + 20% Chlorinated Polyethylene (25% Cl) + 10% Basic Calcium Zinc Molybdate + 2.7% Additives	Class I in ASTM-E-648 testing method	58
Polycapraamide Melt + Mixture of 25 wt% of 4 mol Boric Acid, 1 mol Brominated Pentaerythritol, 0.1 mol Antimony Oxide	LOI 29% Pyrolysis time 30 min Reduction in maximum rate decomposition 17 to 9 mg/min Apparent activation energy of the thermooxidative decomposition process $E_a$ 74.5 kJ/mol (initial material 97.3 kJ/mol)	59
Nylon 6 + 0.6% of 97.7% Red Phosphorus at 230°C	FR properties achieved with self-extinguishing time of 5 s	60

<sup>a</sup>Calcium zinc molybdate ( $\text{CaO} \cdot \text{ZnO} \cdot \text{mMoO}_3 \cdot n\text{H}_2\text{O}$ ); white powder; insoluble in water; density 3 g/cm<sup>3</sup>.

was observed on introduction of borofos, but it does not change the molecular packing coefficient of the nylon 6, which varies from 0.64 (original) to 0.67 (for fiber-containing borofos). The complex salt of an alkyl phosphonic acid and antimony has greater flame-retarding efficiency than fostertrol. The LOI in the case of samples using any of these compounds is 29–30%, while the “phosphorus” present in the complex salt of an alkyl phosphonic acid and antimony is half of the phosphorus present in fostertrol. It is due to antimony-phosphorus synergism taking place in a complex salt of an alkyl phosphonic acid and antimony.

Wells and Cole [57] disclosed in their patent a method for producing flame-retardant nylon 6 fiber that retains good breaking strength. This fiber was prepared by first producing a master batch from 75 parts nylon 6, 15.25 parts chlorinated polyethylene (25% Cl), 7.75 parts KemGard 425 (calcium zinc molybdate), and 2 parts other additives. A mixture of 1:11.5 master batch and nylon 6 was then melt spun. The percentages of zinc, molybdenum, and chlorine in the nylon 6 fiber were 0.01–2.9%, 0.002–0.58%, and 0.05–1.3%, respectively. They also produced flame-retardant nylon 6 by varying the additive levels to 20% chlorinated polyethylene (25% Cl), 10% basic zinc molybdate, and 2.7% other additives, and the product was class I by the ASTM-E-648 testing method [58].

A ternary combustion fire-retardant system consisting of boron, antimony, and bromine was developed by Tyuganova et al. [59]. A 25 wt% mixture of 4 moles boric acid, 1 mole brominated pentaerythritol, and 0.1 mole antimony oxide was introduced into the nylon 6 melt and was spun at a temperature of 235°C on a laboratory melt-spinning rig. There was not much change in the physicomechanical properties. The maximum LOI of the fiber was 29%. A binary system consisting of boric acid and brominated pentaerythritol exhibited an LOI of 25%, but when boric acid has been replaced by antimony oxide, the system exhibited an LOI of 26% (in the modified fiber, the boron content was 2.28%, bromine 3.09%, and antimony 2.61%). It has been suggested that ternary flame retarders of antimony halides or oxyhalides exhibit effective free-radical inhibition on the thermo-oxidative decomposition of the modified polymer. The advantage of the selected flame-retarder system is the absence of acid hydrolysis of the amide bond in the polycapromide and a decrease in the degree of polymerization (DP) during the fiber spinning. The amounts of toxic gases like CO and HCN were also considerably reduced.

Marik and coworkers [60] extruded nylon 6 (water extractable 1.2%, moisture 0.2%, melting temperature 217°C, and DP 150) with 0.6% of 97.7% red phosphorus at 230°C. The fiber showed a self-extinguishing time of 5 s.

#### 4.2.3. Surface Treatment/Topical Finishing

Generally, there is a problem of polymer degradation with the spinning dopes containing flame retardant. Hence, topical finishing or posttreatment commonly are proposed for conferring flame retardancy to nylon fabrics. The treatment of the nylon fabrics with thiourea-based (Fig. 3a) condensation products with formaldehyde or urea, melamine (Fig. 3b), and their methylolated derivatives has generated interest [61]. A number of finishing agents used for nylon fabric are given in Table 5.

Hydroxy methylation of nylon 6 was performed with formaldehyde (36%) at 70°C–80°C and at a pH of 0.9–1 for 1–2 h. This was followed by treatment with pyrovatex CP (*N*-methylol dimethyl phosphonopropionamide) (10–50%) for 5–30 min and drying at 150°C–180°C for 2–6 min. The product has an LOI of 31.4%, while nylon 6 treated only with formaldehyde gave an LOI value of 23.6% [62].

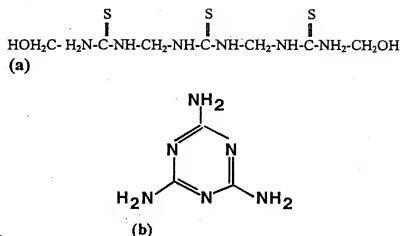


FIG. 3. (a) Methylol thiourea; (b) melamine (2,4,6-triamino-1,3,5-triazine).

Efros et al. [63] treated the nylon 6 fiber with the solution of boric acid polyester (BAP) (Fig. 4) containing boron, chlorine, and nitrogen. The best flame-proofed properties of nylon 6 fibers were attained at a chlorine/boron ratio of 3:20 and a nitrogen/boron ratio of 1:4 in the BAP. The treated fiber has an LOI of 28.2%. The maximum decomposition rate of BAP-treated nylon 6 fiber is reduced from 16 to 6.5 mg/min. In BAP-treated fiber, the yield of caprolactam during the pyrolysis process is reduced almost three times, and this ensures the increase in fire resistance.

Flame-retardant nylon fabric was also produced by treatment with an aqueous solution containing 18.3% Tetrakis Hydroxymethyl Phosphonium Chloride (THPC), 8.5% trimethylol melamine (TMM), 8.8% urea, and 0.1% of a surfactant [64–68]. It was applied on to the fabric by a pad-dry-cure method in which drying was done at 110°C and curing at 145°C. At this temperature, THPC polymerizes with TMM with the evolution of hydrochloric acid. Urea is employed to tie up this hydrochloric acid.

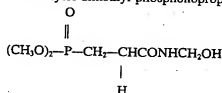
Cross-linkable organophosphorus compounds based on 1,3,5-triacryloylhexa hydro-1,3,5-triazine and dialkyl phosphine oxide have also been used as flame-retardant finishes for polyamides [69]. Novolak or epoxy resins containing 1.7% red phosphorus have also been reported as a flame-retardant finish for nylons [70].

El-Garf and El-Kemry [71] modified the nylon 6 fiber by treating with 2,5-dichlorobenzenesulfonyl chloride (DBSC), which had a great effect on heat and chemical stability of the fibers. They obtained the best results with a DBSC concentration of 25%, a reaction temperature of 115°C, and a treatment time of 4 h. It was found that increasing the DBSC concentration and temperature was more effective because of the increase in sulfur content in modified fibers than increasing the reaction time. Thus, the modified fiber contained 4.9% sulfur and 26.4% carbon residue (a measure of flame retardancy) and had a 97.5% degree of crimp. It also lost solubility in formic acid, concentrated mineral acids, and aqua regia. The fibers only glowed and charred without losing fiber form when put in direct flames, and there was no melting up to 1000°C. The activation energy of decomposition  $\Delta E$  was 194 kJ/mol compared to 46 kJ/mol for the unmodi-

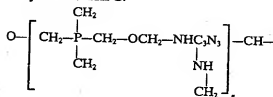
TABLE 5  
Surface Treatment/Topical Finishing

Finishes	Properties	Reference
Treatment with HCHO (36%) + 10.50% Pyrovatex CP <sup>a</sup>	LOI 31.4%	62
Treatment with boric acid polyesters (BAP)	LOI 28.2% Relative breaking load 36.8 CN/tex vs. 44.4 CN/tex of untreated Decomposition rate of fiber reduced from 16 to 6.5 mg/min	63
Treatment with 18.5% THPC <sup>b</sup> + 8.5% trimethylol melamine (TMM) + 8.8% urea + 0.1% of surfactant	FR properties achieved	64-68
Treatment with cross-linkable organophosphorus compounds based on 1,3,5-triacryloylhexahydro-1,3,5-triazine and dialkyl phosphine oxide	FR properties achieved	69
Treatment with Novolak or epoxy resins containing 1-7% red phosphorus	FR properties achieved	70
Treatment with 25% 2,5-dichlorobenzenesulfonyl chloride at 115°C for 4 h	Activation energy of decomposition $\Delta E$ 194 kJ/mol No melting up to 1000°C Glowed and charred without losing fiber form, 10% loss in tenacity	71
Phosphorylation of polyamide	Decomposition temperature 350°C Melting temperature 258°C-270°C	75

<sup>a</sup>N-Methylol-dimethyl phosphonopropionamide [92]:



<sup>b</sup>Polymerized THPC:



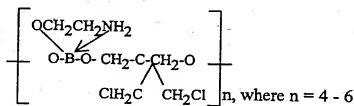


FIG. 4. Boric acid polyester.

fied fibers. However, there was about 10% loss in strength properties, specifically tenacity, which could be due to chemical degradation. The fire resistance of the treated fiber is due to the introduction of an aromatic ring containing sulfur into the polyamide polymer chain, cross-linking of the fibers, or cyclization of the polyamide [72-74]. Belgium [75] revealed that, when polyamide is phosphorylated, its melting temperature increases from 258°C to 270°C, and the decomposition temperature increases to 350°C.

#### 4.3. Manufacture of Flame-Retardant Nylon Plastics

Nylon plastics are commonly used in the composite field as reinforcement thermoplastics and also are used as cables in the electrical and electronic industries. Flammability of nylon plays a crucial role in these fields, too. Hence, it is worthwhile to know the additives used to impart flame retardancy on the thermoplastic nylons.

The flammability tests in the textile industry are completely different from those used for reinforced plastics. A better method of evaluation for materials used in the electrical industry involves the use of Underwriters Laboratories Subject 94 Test [76].

The test method is described [77, 78] as placing a sample (127 × 13 × 3 mm) vertical to a small Bunsen burner flame for 10 s; the sample is ignited at the bottom and burns. If the specimen self-extinguishes within 30 s, another 10-s application is made. Flaming droplets are allowed to fall on a dry absorbent surgical cotton located 300 mm below the sample. The rating is then made as follows:

UL-94, V-0: The average burning time is less than 5 s, and the drips do not ignite the cotton.

UL-94, V-1: The time is less than 25 s, and the drips do not ignite the cotton.

UL-94, V-2: The sample is extinguished, but the cotton is ignited.

The various additives used in flame-retardant nylon plastics are given in Table 6. The high amounts of additive adversely affect the crystallinity of nylon polymers, which is an essential parameter for fiber formation. In nylon 6, the amide linkage is quite reactive, and this is the site where often the flame-retardant additive interaction occurs [79]. This prevents the use of many flame-retardant polyamides for spinning into fibers, and they can be only used for preparing moldings. There is a wide range of flame-retardant additives for polyamide plastics, most of which are used before extrusion of the polymer melt.

Hochberg and Mason [80] prepared a flame-retardant nylon composition by blending 81.45 parts nylon 6 (80% amine terminated) with 14 parts poly(pentabromo benzyl acrylate), 3.5 parts antimony oxide, 0.05 parts calcium chloride, 0.25 parts potassium iodide, and 0.75 parts zinc stearate, and then the mixture was extruded. The prepared

flame-retardant nylon composition showed a UL-94 flammability rating V-0, while nylon with 50% terminal amine groups gave a rating of V-2.

Nylon 6 was blended at 125 parts to 13.6 parts  $\text{Ph}_2\text{Si}(\text{OH})_2$  (and/or a low molecular weight phenyl-substituted siloxane diol), 6.8 parts magnesium stearate, 27.4 parts aluminum trihydrate (ATH), and 20.6 parts deca bromodiphenyl oxide (DBDPO), conditioned in boiling water for 2 h, and placed under ambient conditions for 2 days; it had a UL-94 rating of V-0 and a self-extinguishing time of 4.8 s [81].

Nylon 6 mixed with 20% ammonium polyphosphate (APP) and talc showed a UL-94 rating of V-O [82]. A chemical reaction of APP with talc was detected in the mixture above 350°C, which prevents the volatilization of polyphosphoric acid.

The effect of the fire-retardant APP on the thermal decomposition of aliphatic nylon 6 was studied by Levchik et al. [83]. They described that the intumescent behavior induced by APP in mixtures with nylon 6 is responsible for its fire-retardant action. From the thermal analysis results, it was observed that an intumescent char was formed on the surface of the burning specimen even in the presence of as little as 10% APP. Further, it showed that the presence of APP destabilizes nylon 6 and modifies its thermal degradation behavior by lowering the activation energy. From this study, they concluded that APP is an ineffective fire retardant at concentrations below 30% in nylon 6, but increasing the concentration to 40% increases the LOI from 23% to 40% and induces intumescent behavior in the burning material. APP favors the formation of caprolactam as the major volatile product against chain fragments, but it does not seem to increase the yield of residue, which is thermally stable at 550°C. The composition of volatile combustible products obtained from nylon 6 is modified by the presence of APP; however, the amount of volatile product is not affected.

In a patent, Pohl [84] disclosed the method of producing a flame-retardant polyamide composition with good mechanical properties by mixing nylon 6 with the lubricant calcium stearate, the fire-proofing agent melamine cyanurate, and glass fibers in an extruder. A reinforced flame-retardant polyamide composition was also prepared by Williams Jan [85] with nylon 6.6-nylon 6 copolymer (90:10) 53%, glass fibers 20%, melamine sulfate 20%, chlorocyclopentadiene-cyclo-octadiene condensation adduct (dechlorane plus) 4%, and zinc borate 3%. The total composition was mixed and extruded at 250°C–270°C. The UL-94 rating for the specimen was V-0. Another patent [86] described flame-retardant polyamide prepared from adipic acid-caprolactam HMD polymer by the addition of 25 parts melamine cyanurate, 3 parts dechlorane plus, 1 part antimony oxide, and 20 parts glass fiber. The resultant polyamide shows a rating of V-0 in the UL-94 test and an LOI of 27%.

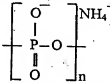
Horacek and Reichenberger [87] added a mixture of two additive dicyanadiamide and melamine to the polyamides (e.g., nylon 6, nylon 6.6, nylon 12) to increase the fire resistance without affecting the mechanical properties or appearance. Ceric et al. [88] produced flame-resistant polyamide by adding antimony oxide and stannous chloride to poly-ε-caprolactam melt.

Grundman et al. [89] produced a flame-retardant polyamide composition by blending 84 parts nylon 6 with 12 parts of 3,4,5,6-tetrabromo-*N*-(2,4-diamino-1,3,5-triazine-6-YL) phthalimide and 4 parts of antimony pentoxide. The flame-retardant polyamide produced showed V-0 rating in the UL-94 test, but when antimony pentoxide was not added to the composition, the resultant flame-retardant polyamide exhibited a V-2 rating in the UL-94 test. Another flame-retardant [21] nylon 6 was prepared with 79% nylon 6, 15% dechlorane, 4% Flamtard S (Alcan Chemicals Ltd., Chalfont Park, Bucks, Eng-

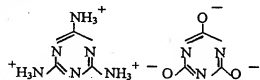
TABLE 6  
Manufacturing of Flame Retardant Nylon Plastics

Reagents	Properties	Reference
81.45 parts Nylon 6 (80% Amine Terminated) + 14 parts Poly(Penta Bromo Benzyl Acrylate) + 3.5 parts $\text{Sb}_2\text{O}_3$ + 0.05 parts $\text{CaCl}_2$ + 0.25 parts KI + 0.75 parts Zinc Stearate <sup>a</sup>	UL 94 rating V-0 vs. V-2 using nylon with 50% amine terminated	80
125 parts Nylon 6 + 13.6 parts $\text{Ph}_2\text{Si}(\text{OH})_2$ (and/or a low molecular weight Phenyl-Substituted Siloxane Diol) + Magnesium Stearate <sup>b</sup> 6.8 parts + 27.4 parts $\text{ATH}^c$ + 20.6 parts DBDPO <sup>d</sup>	UL 94 rating V-0 Self-extinguishing time 4.8 s	81
Nylon 6 + 20% APP + Talc	UL 94 rating V-0	82
40% APP <sup>e</sup> + Polyamide 6	LOI 40% Thermally stable up to 550°C	83
Nylon 6 + calcium stearate + Melamine Cyanurate <sup>f</sup> + Glass fiber	Good mechanical properties	84
53% Nylon 6.6-Nylon 6 (90:10) + Glass fibers 20% + Melamine Sulfate 20% + Dechlorane Plus <sup>g</sup> 4% + Zinc Borate ( $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ ) 3%	UL 94 rating V-0	85
Adipic Acid-Caprolactum-HMD Copolymer + 20 parts Glass fibers + Melamine Cyanurate 25 parts + 3 parts Dechlorane Plus + 1 part $\text{Sb}_2\text{O}_3$	UL 94 rating V-0 LOI 27% Tensile strength 123 MN/m <sup>2</sup>	86
Nylon 6/Nylon 6.6/Nylon 12 + Dicyandiamide <sup>h</sup> + Melamine <sup>i</sup>	No change in mechanical properties and appearance	87
Poly $\xi$ -caprolactum + $\text{SnCl}_2$ + $\text{Sb}_2\text{O}_3$	FR properties achieved	88
84 parts Nylon 6 + 12 parts 3,4,5,6-Tetrabromo-N-(2,4-Diamino-1,3,5-Triazine-6-YL) Phthalimide + 4 parts $\text{Sb}_2\text{O}_3$	UL 94 rating V-0	89
79% Nylon 6 + 15% Dechlorane + 4% Flamtard S <sup>j</sup> + 2% Zinc Borate	UL 94 rating V-0	21
Nylon 6 + 15-20% Poly ( <i>p</i> -Phenylene sulfide) (PPS)	Enhanced tensile and flexural properties	90
Nylon 6 + Magnesium Sulfate + $\text{Sb}_2\text{O}_3$ + Zinc Oxide/ Zinc Borate/Ferric Oxide/Iron Oxide/Zinc Stannate/ Zinc Molybdate	FR properties achieved	91

<sup>a</sup> $(\text{CH}_3(\text{CH}_2)_{16}\text{COO})_2\text{Zn}$ , mp 125°C; <sup>b</sup> $(\text{CH}_3(\text{CH}_2)_{16}\text{COO})_2\text{Mg}$ , mp 145°C; <sup>c</sup>Decomposes above 230°C [93]; <sup>d</sup>Br content 83%, mp 295°C-305°C, decomposition point ca. 425°C [94].

<sup>e</sup>  white powder, starts decomposing at 250°C,  $n > 100$ , commercially known as PHOS-CHECK4, P 32%, N 15.7%, H 4% [96, 97].

<sup>f</sup> Melamine cyanurate:



<sup>g</sup>Hooker Chemical Corp., mp 480°C [98]; <sup>h</sup>mp 208°C-211°C,  $(\text{H}_2\text{N})_2\text{C}=\text{NCN}$ ; <sup>i</sup>mp 347°C; <sup>j</sup>Alcan Chemicals Ltd., Chalfont Park, Gerrards Cross, Bucks, England.



land), and 2% zinc borate. In this case, flame-retardant rating was V-0 on the UL-94 test.

Srinivasan, Vasantha Kumari, and Uthaih [90] incorporated 15–20% poly(*p*-phenylene sulfide) (PPS) in nylon 6, which provided flame-retardancy and enhanced the tensile and flexural properties. PPS is characterized by its good heat, flame, and chemical resistance, as well as electrical insulation properties. It has been observed that magnesium sulfate, antimony oxide, and zinc oxide/zinc borate/ferric oxide/iron oxide/zinc stannate/zinc molybdate also provide flame retardancy to nylon 6 [91].

## 5. SUMMARY

Flame retardancy in nylon fiber and plastics was studied. The effect of various flame-retardant chemicals during the polymerization, spinning, and finishing stages has been thoroughly investigated to select suitable processes and chemicals for flame retardancy of nylon 6 or nylon 6.6 fibers. Generally, phosphorus-based compounds are added during the polymerization stage to achieve flame-retardant nylon fibers. Red phosphorus and magnesium oxide addition during the polymerization stage of nylon 6 polymer gives a fiber with good flame retardancy and an LOI of 28.5%. The flame-retardant additive for addition at the spinning dope stage has to be stable at the melt spinning temperature, so the choice of chemicals becomes limited. The use of a complex compound of an alkyl phosphonic acid and antimony at the spinning dope stage gives flame-retardant nylon fiber having an LOI of 29–30%. The addition of chlorinated polyethylene and zinc molybdate in the spinning dope was also found effective. An interesting effect is seen when a boric acid, brominated pentaerythritol, and antimony trioxide combination was added in a spinning dope of nylon 6; the resultant flame-retardant fiber had an LOI of 29%, but if any of the compound was not added, the LOI was reduced to 25–26%. The high thermal stability required for the flame-retardant additives may be dispensed with using surface finishing, which is supposed to be a more convenient and easier method. In this method, the choice of chemicals becomes wide. The treatment with thiourea-based condensation products is very popular for flame retardancy of nylon fabric. The other effective method is hydroxymethylation of nylon fabric with formaldehyde, followed by treatment with pyrovatex CP. It gives an excellent flame retardancy to nylon and an LOI of 31.4%.

Nylon plastics may be rendered flame retardant by the addition of poly(pentabromo benzyl acrylate), antimony oxide, small amounts of calcium and potassium halides, and zinc stearate in the polymer mixture before extrusion. Addition of aluminum trihydrate and DBDPO was also effective for the purpose. Nylon 6–nylon 6.6 copolymer may be made flame retardant by addition of glass fiber, melamine sulfate, chlorocyclopentadiene-cyclo-octadiene, and zinc borate.

Recent awareness regarding the environment has led to a search for eco-friendly flame-retardant chemicals. Some eco-friendly chemicals like APP and poly(vinyl alcohol) have emerged as low-hazard flame retardants for nylon plastics, but the use of these flame retardants for fibers could become infeasible due to their adverse effect on rheological properties of the polymer and, in turn, fibrillization. Therefore, the search for an eco-friendly flame retardant for nylon fibers needs more effort.

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